ENERGETIC MATERIALS FROM CUBANE

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Summary: New generations of highly energetic materials are required for the modern Navy. Cubane is a very dense, exceptionally energetic hydrocarbon; its heat of formation, density, and strain energy are all extraordinarily high -- in combination unexceeded by any other stable hydrocarbon. This dense, energetic system has 8 identical methine C-H groups at which hydrogen may be replaced by energy-rich substituents. The goal of this project is to understand the fundamental properties of the basic set of reactive intermediates that might be used for the functionalization of the cubane nucleus. Only cubane-1,4-dicarboxylic acid is available readily. Ways to introduce other substituents elsewhere on the cubane nucleus are needed. As cubanes are far from the ordinary in their chemical behavior, this necessitates the development of radically new methodology.

The enormous strain energy in the cubane system (+161 kcal/mole) makes cubanes very different chemically from ordinary compounds. New reactions have been invented, special reagents have been developed, and novel methods for functional group transformations have been found to provide for systematic elaboration of the cubane system.

In the course of this work we have characterized cubyl anion, cation (the least likely carbonium ion), and radical. We have developed methodology for using each of these as intermediates in the synthesis of new cubanes. We have worked out the chemistry of cubyl carbinyl systems, including the radical (the fastest rearranging alkyl radical), anion and cation. We have prepared cubene, the most pyramidalized olefin, and 1,9-homocubene, the most twisted olefin. We discovered 1,4-cubanediyl, a new kind of organic intermediate. We have prepared and started the characterization of a completely new kind of rigid rod polymer. We have developed amide-activated ortho-metalation technology for the functionalization of strained systems. We have applied this to practical synthesis of important aromatic compounds. We discovered ortho-magnesiation, an environmental satisfactory method for metalation of aromatics. We have put the fundamental chemistry of the cubane system "on the map". It is now ready for inclusion into organic textbooks.

In the course of our ONR-sponsored work on the cubane system, there has been a rich fall-out applicable to non-ONR problems. This has permitted us to introduce new methodology for the synthesis of the important, heat-stable polyimide resins; to prepare polycubanes designed to be liquid ferroelectric crystal switches, to open the possibility of using cubanes to approach stabilized polyacetylene semiconductors, and to start work on the evaluation of substituted cubanes as antiviral agents. We have prepared many new cubanes. Forty-one of these have been submitted to the National Cancer Institute for screening against AIDS and various malignant tumors. To date, 11 compounds have shown interesting activity, sufficient to merit additional testing.

Technical Reports: Publications (copies attached) have been submitted in lieu of technical reports. A list follows:

Oxidative Deiodination of Cubyl Iodides: A Tactic for the Nucleophilic Introduction of Substitutents onto the Cubane Framework
Tetrahedron Letters, **1986**, *27*, 6055, with G. Cunkle

Reverse Transmetalation: A Strategy for Obtaining Certain Otherwise Difficultly Accessible Organometallics
J. Am. Chem. Soc., **1987**, *109*, 948, P. E. Eaton, G. T Cunkle, G. Marchioro and R. M Martin

Synthesis of Zinc, Cadmium, Tin and Silicon Derivatives of Cubane.
Tetrahedron Letters, **1987**, *28*, 1055, P. E. Eaton, H. Higuchi and R. Millikan

Synthesis of Cubane Based High Energy Materials
SPIE Vol. 872 Propulsion, **1988**, 30, R. J. Schmitt and J. C. Bottaro, and P. E. Eaton

X-ray Structures of Cubylcubane and 2-*tert*-Butylcubylcubane: Short Cage-Cage Bonds
J. Am. Chem. Soc., **1988**, *110*, 7232, R. Gilardi, P. E. Eaton, and M. Maggini

Conversion of Isocyanates to Nitro Compounds with Dimethyldioxirane in Wet Acetone
J. Org, Chem., **1988**, *53*, 5353, P. E. Eaton, G. W. Wicks

Magnesium Amide Bases and Amido-Grignards. Part I: Ortho Magnesiation
J. Am. Chem. Soc., **1989**, *111*, 8016, P. E. Eaton, C. -H. Lee and Y. Xiong

Synthesis of Iodocubanes by Decarboxylative Iodination
Tetrahedron Letters **1989**, *30*, 6967, P. E. Eaton, J. Tsanaktsidis

The Reactions of 1,4-Dihalocubanes with Alkyllithiums. The Case for 1,4-Cubadiyl
J. Am. Chem. Soc. **1990**, *112*, 876 , P. E. Eaton, J. Tsanaktsidis

The Mechanism of the Olefin-to-Carbene Rearrangement for 9-Phenyl-1(9)-homocubene
J. Org. Chem. **1990**, *55*, 1321, P. E. Eaton, A. J. White.

HBr Cleavage of Cubane-1,4-dicarboxylic Acid. Easy Entry into the Nortwistbendane(ene) System
J. Org. Chem. **1990**, *55*, 2823, P. E. Eaton, R. Millikan

An Improved Preparation of 9-Oxabicyclo[3.3.1]nona-2,6-diene
Synthesis **1990**, 483, P. E. Eaton, R. Millikan

Cubyl Cation
J. Am. Chem. Soc. **1990**, *112*, 3225, P. E. Eaton, C.-X. Yang and Y. Xiong

Automerization of Homocubylidene: Proof of a Reversible Olefin/Carbene Rearrangement
J. Am. Chem. Soc. **1990**, *112*, 4055, P. E. Eaton, R. B. Appell

Isomerization of the Cubane Radical Cation to Bridged 1,4-Bishomobenzene (Bicyclo[3.4.0]octa-2,6-diene-4,8-diyl) Radical Cation
J. Am. Chem. Soc. **1990**, *112*, 4567 X.-Z. Qin, A. D. Trifunac, P. E. Eaton,and Y. Xiong

Bond Lengths and Quadratic Force Field for Cubane
J. Am. Chem. Soc. **1991**, *113*, 1514 L. Hedberg, H. Hedberg, P. E. Eaton, N. Nodari and A G. Robiette

Regiospecific Oxidation of Binor S and a New Pentacyclotetradecane System
*J. Org. Chem.***1990**, *55*, 6105, P. E. Eaton, K. Pramod

Cubanourea. The First Fused-ring Cubane
J. Org. Chem. **1990**, *55*, 5746 P. E. Eaton, K. Pramod

Cubane Radical Cation in Liquid Hydrocarbons: Time-resolved Fluorescence Detected Magnetic Resonance Study
*J. Am. Chem. Soc.***1991**, *113*, 670 X.-Z. Qin, A. D. Trifunac, P. E. Eaton, and Y. Xiong

Synthesis of AlkynylCycloöctatetraenes and Alkynylcubanes
J. Org. Chem.1991, 56, 5138-5142 P. E. Eaton and D. Stössel

On the Discovery of Direct ortho-Magnesiation
J. Chinese Chem. Soc. (Taiwan) **1991** *38*, 303-306 P. E. Eaton, Y. Xiong and C.-H. Lee

The Preparation and Fate of Cubylcarbinyl Radicals
J. Am. Chem. Soc. **1991**, *113*, 7692-7697 P. E. Eaton, Y. C. Yip

Regiospecific Functionalization of Binor S by a Gif Type Oxidation System.
Tetrahedron Letters **1991**, *32*, 6263-6264 with D. H. R. Barton, and W.-G. Liu

On the Nature of Cubyl Cation.
J. Am. Chem. Soc. **1992** *114*, 3118, with J. P. Zhou

Systematic Substitution on the Cubane Nucleus: Steric and Electronic Effects.
J. Org. Chem., **1992**, *57*, 4277-4281 with X. Yiong and J. P. Zhou

Systematic Substitution on the Cubane Nucleus. Synthesis of 1,3,5-Trinitrocubane and 1,3,5,7-Tetranitrocubane
J. Org. Chem., **1992**, in prep, with Y. Xiong and R. Gilardi

Picosecond Radical Kinetics. Bond Cleavage of the Cubylcarbinyl Radical.
J. Am. Chem. Soc. **1992**, *114*, 6326-6329 with S.-Y. Choi, M. Newcomb and Y. C. Yip

Cubane: Starting Material for the 1990s and the New Century.
Angewandte Chemie International Edition **1992**, *32*, 1421-1436